Wednesday, May 13
Facility-specific Workshops

APS Workshop 11
Tracking Electronic and Structural Dynamics in Proteins and Materials at Sector 14

Location: Bldg. 402, Room E1100/E1200

Organizers: Robert Henning (CARS, University of Chicago) and Anthony DiChiara (APS and CARS, University of Chicago)

The major upgrade to the BioCARS 14-ID beamline [1] produced unprecedented time-resolved capabilities that have been exploited for x-ray science spanning biology, chemistry, materials science, and physics. More recently, a new area detector (Rayonix MX340-HS, a 60-megapixel high-readout-rate integrating area detector) and secondary Kirkpatrick-Baez focusing mirrors were installed. The new equipment expands opportunities for time-resolved x-ray diffraction and solution scattering at 14-ID even further, by providing ~15 × 15 μm^2 focused pink or monochromatic beam.

The workshop will bring together current practitioners and prospective new users of time-resolved pump-probe x-ray techniques from both biological and physical sciences. The goal of the workshop is to provide an overview of current capabilities and to discuss future challenges, needs, and opportunities, especially as they relate to brighter and smaller spots offered by the reduced-emittance APS MBA-lattice upgrade. The scientific emphasis will be on our new/current focal capability and the recent advances in serial crystallography, microcrystallography, x-ray excited warm dense matter, and time-resolved Laue diffraction and solution scattering.

Reference

[1] T. Graber et al., *J. Synch. Rad.* **18**, 658 (2011).

1:30 – 1:40 Robert Henning (University of Chicago/BioCARS)
Introduction

1:40 – 2:10 Hyun Sun Cho (National Institutes of Health)
Watching a Signaling Protein Function in Real Time via 150-picosecond Time-resolved Solution Scattering

2:10 – 2:40 Xiaoshan Xu (University of Nebraska-Lincoln)
Structural Dynamics in Improperly Multiferroic Hexagonal Ferrites

2:40 – 3:10 Marius Schmidt
Time-resolved Macromolecular Crystallography at the Synchrotron and at the X-ray FEL

3:10 – 3:30 Break

3:30 – 4:00 Stephen Durbin (Purdue University)
Interaction of X-ray and Laser Pulses in GaAs

4:00 – 4:30 Sebastian Westenhoff (University of Gothenburg, Sweden)
Signal Transduction in Phytochrome Photosensors Visualized by Time-resolved X-ray Scattering

4:30 – 5:00 Aaron Lindenberg (Stanford University/SLAC)
Ultrafast Studies of Interlayer Coupling in Transition Metal Dichalcogenide ReS2

5:00 Concluding remarks

WK11

Watching a Signaling Protein Function in Real Time via 150-picosecond Time-resolved Solution Scattering

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To understand how signaling proteins function, it is crucial to know the time-ordered sequence of events that lead to the signaling state. Using the time-resolved infrastructure we helped develop on the BioCARS beamline, we tracked the reversible photocycle of photoactive yellow protein following trans-to-cis photoisomerization of its p-coumaric acid (pCA) chromophore. Briefly, a picosecond laser pulse photoexcites pCA and triggers a structural change in the protein, which is probed with a suitably delayed picosecond x-ray pulse. When the protein is studied in a crystalline state, this "pump-probe" approach recovers time-resolved diffraction "snapshots" whose corresponding electron density maps can be stitched together into a real-time movie of the structural changes that ensue. However, the actual signaling state is not accessible in the crystalline state due to crystal packing constraints. This state is accessible in time-resolved small- and wide-angle x-ray scattering studies, which probe changes in the size, shape, and structure of the protein. The mechanistically detailed, near-atomic resolution description of the complete PYP photocycle developed from these studies provides a framework for understanding signal transduction in proteins, and for assessing and validating theoretical/computational approaches in protein biophysics. Thanks to an NIH-funded 2014 upgrade of the BioCARS beamline, the x-ray flux achievable and the rate at which images can be acquired has been boosted significantly, benefitting both time-resolved Laue crystallography and time-resolved SAXS/WAXS studies. This research was supported in part by the Intramural Research Program of the NIH, NIDDK.

WK-11

Structural Dynamics in Improperly Multiferroic Hexagonal Ferrites

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Hexagonal ferrites, as a new family of multiferroic materials, exhibit ferromagnetism and ferroelectricity simultaneously. The improper ferroelectricity appears below 1050 K, driven by a non-polar structural distortion, while the weak ferromagnetism occurs below 130 K resulting from a competition between a couple of structural distortions. Since both the ferroelectricity and ferromagnetism have structural origins, a structurally mediated magnetoelectric coupling may be possible, as proposed by theory. As a key step, understanding the structural response to an electric field is crucial to understanding the magnetoelectric couplings in hexagonal ferrites. Using time-resolved x-ray diffraction, we probe the structural response to an effective electric field generated by the photo-induced charge carriers. By comparing the results with temperature-dependent structural refinements, dramatic responses of non-polar structural distortion are revealed, with the same time-scale of the charge carrier decay. The pattern of the lattice constants change indicates complex nature of the structural response. These results suggest that the structural response to the electric field may be a route for the magnetoelectric effect.

WK11

Time-resolved Macromolecular Crystallography at the Synchrotron and at the X-ray FEL

Marius Schmidt

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Time-resolved crystallography unifies structure with kinetics. A time-series of difference maps is required to extract the molecular structures of reaction intermediates as well as the temporal evolution of the associated concentrations. Powerful synchrotron beamlines such as BioCARS at the Advanced Photon Source (APS) make the collection of these movies possible. *Multiple* time-series of photoactive yellow protein (PYP) can be collected rapidly. An additional experimental parameter such as the temperature can be varied. New, hitherto inaccessible, information can be extracted. Crystallography becomes five-dimensional [1,2]. At an x-ray free-electron laser, however, time-resolved serial femtosecond crystallography (TR-SFX) has several advantages: (i) due to the diffraction before destruction principle, radiation damage is negligible although enormous doses are deposited, (ii) small nano- and micro-crystals are utilized that can be easily and uniformly excited. Reactions in photo-reactive proteins such as PYP can be started by an optical laser pulse, and reactions in enzymes may be started by diffusion of substrate, (iii) cyclic reactions as the one in PYP and non-cyclic reaction such as those catalyzed by enzymes are conceptually on the same footing, (iv) the ultra-short, femtosecond x-ray pulses provide access to ultrafast time-scales beyond the pulse-limitations at the synchrotron. We present difference maps determined from TR-SFX [3] at beamline CXI at the LCLS. These results will pave the way to exciting, new experiments with photoreceptors and enzymes with serial crystallography at synchrotrons at the x-ray FELs.

[1] Schmidt, M., Srajer, V., Henning, R., Ihee, H., Purwar, N., Tenboer, J., and Tripathi, S., (2013), Protein energy landscapes determined by five-dimensional crystallography, *Acta Crystallogr D* **69**, 2534–2542.

[2] Schmidt, M., Graber, T., Henning, R., and Srajer, V., (2010), Five-dimensional crystallography, *Acta crystallographica. Section A, Foundations of crystallography* **66**, 198–206.

[3] Tenboer, J., Basu, S., Zatsepin, N., Pande, K., Milathianaki, D., Frank, M., Hunter, M., Boutet, S., Williams, G.J., Koglin, J.E., Oberthuer, D., Heymann, M., Kupitz, C., Conrad, C., Coe, J., Roy-Chowdhury, S., Weierstall, U., James, D., Wang, D., Grant, T., Barty, A., Yefanov, O., Scales, J., Gati, C., Seuring, C., Srajer, V., Henning, R., Schwander, P., Fromme, R., Ourmazd, A., Moffat, K., Van Thor, J.J., Spence, J.C., Fromme, P., Chapman, H.N., and Schmidt, M., (2014), Time-resolved serial crystallography captures high-resolution intermediates of photoactive yellow protein, *Science* **346**, 1242–1246.

WK11

Interaction of X-ray and Laser Pulses in GaAs

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Unusual excited states of matter can now be created with x-ray pulses at the APS Sector 14, a unique synchrotron source, creating energy densities comparable to optical laser pulses but with unique properties driven by the greater penetration depth and an energetic spectrum of electrons and fluorescence. An x-ray-induced excited state can be further excited by a laser pulse, or an x-ray pulse can excite a previously laser-pumped material. Combining the strikingly different interaction with materials of x-rays and optical photons can lead to new metastable states with unique dynamical properties, such as x-ray induced optical transparency. We report here on a double pump study of GaAs, using an x-ray pump with photons energetic enough to eject *K* electrons in GaAs, and an optical laser pump tuned for exciting valence electrons into the conduction band. Optical probes reveal that defect states surprisingly play a critical role in mediating strong interactions between the x-rays and the optical photons.

WK11

Signal Transduction in Phytochrome Photosensors Visualized by Time-resolved X-ray Scattering

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Sensory proteins must relay structural signals over large distances from the sensory site to regulatory output domains. Phytochromes are a major family of sensor proteins that control diverse cellular functions in plants, bacteria and fungi.

We study the structural dynamics of signal transduction in the photosensory core of the phytochrome form *Deinococcus radiodurans*. Our crystal and solution structures show an open and closed form of the dimeric protein for the activated and resting states, respectively [1]. This nanometer-scale rearrangement is controlled by refolding of an evolutionarily conserved 'arm', which is in contact with the chromophore. Time-resolved x-ray solution scattering data confirms that the opening movement is conserved in many bacterial phytochromes [2].

To arrive at these conclusions, x-ray crystallography was paired with time-resolved solution scattering. I will discuss two approaches to extract structural information from the latter data set. Firstly, structures are selected from many frames in unbiased molecular dynamics simulations [1,3]. Secondly, we have programmed a GROMACS-based molecular dynamics tool, in which the molecules are driven towards states that agree with the experimental scattering data [4]. I will discuss how these tools open up for studying the structural changes of proteins in solution.

[1] Takala, H. et al., Signal amplification and transduction in phytochrome photosensors. *Nature* **509**, 245–248 (2014).

[2] Björling, A. et al., Ubiquitous structural signalling in bacterial phytochromes. Unpublished.

[3] Arnlund, D. et al., Visualizing a protein quake with time-resolved x-ray scattering at a free-electron laser. *Nat. Methods* **11**, 923–926 (2014).

[4] Björling, A., Niebling, S., Marcellini, M., van der Spoel, D., and Westenhoff, S. Deciphering solution scattering data with experimentally guided MD simulations. *J. Chem. Theory Comput.* **11**, 150113180629009 (2015).

WK11

Ultrafast Studies of Interlayer Coupling in Transition Metal Dichalcogenide ReS2

Aaron M. Lindenberg

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I will describe recent experiments probing ultrafast structural dynamics in quasi-2D transition metal dichalcogenides. Time-resolved x-ray scattering measurements carried out at Sector 14 at the APS and at the Stanford Synchrotron Radiation Laboratory (SSRL) allow for direct probes of interlayer coupling phenomena in these materials, a key aspect of their functionality. Measurements reveal ultrafast acoustic responses and induced out-of-plane disorder following above-gap photo-excitation. If time allows, I will also describe recent complementary studies using time-resolved electron diffraction.